

# A preliminary DFT study of the adsorption and dissociation of $CH_4$ , $SO_2$ and $O_2$ reactions on $Cr_2O_3(0001)$

S. N. Hernández Guianca<sup>a</sup>, D. Coria<sup>b</sup>, I. M. Irurzun<sup>\*,c</sup>, E. E. Mola<sup>1</sup>.

December 5, 2016

<sup>a</sup>Facultad de Química, e Ingeniería, Pontificia Universidad Católica Argentina, Mendoza 4197 CP 2000 Rosario, Argentina.

<sup>b</sup>Universidad del Centro Educativo Latinoamericano. Av. Pellegrini 1332 CP 2000 Rosario, Argentina.

<sup>c</sup>CCT La Plata – CONICET. Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata. Diagonal 113 y 64, CP (1900), La Plata, Argentina. Telephone: +54 221 425 74 30, ext. 149. Fax: +54 221 425 46 42.

\*Corresponding Author

<sup>1</sup> In memory

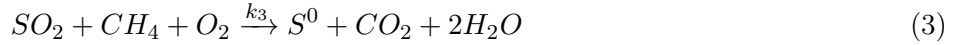
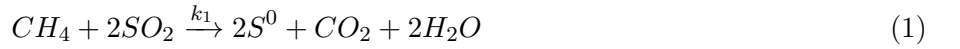
## Abstract

In the present work, we study the structures and molecular geometries of  $CH_4$ ,  $SO_2$  and  $O_2$  adsorbed on  $Cr_2O_3(0001)$ . Using computational calculations based on the density functional theory (DFT), we analyze the most suitable sites to carry out the adsorption of each of the molecules mentioned, and the influence of each species on the adsorption and dissociation of the others. The results allow us to understand the activation of the  $Cr_2O_3(0001)$  surface, which leads to the presence of  $SO_2$  during the oxidation of  $CH_4$ , as was experimentally verified.

## 1 Introduction

Transition metal oxide surfaces have been a major focus of interest in the field of catalysis and corrosion. Environmental sciences have paid much attention to catalytic surfaces, which have been used to remove pollutant molecules, such as  $SO_2$ ,  $CH_4$ ,  $CO$ , and  $CO_2$ , from the atmosphere. Among these molecules,  $SO_2$

is one of the products from natural and anthropogenic sources emitted to the atmosphere that may turn into acid rain. Most of the  $SO_2$  released into the atmosphere ( $\approx 3/4$ ) is produced by human activities, especially by the combustion of fossil fuels. More than half of the world production comes from a few developed countries. In industrial stacks,  $SO_2$  reduction occurs by reaction with  $CH_4$ , which is then oxidized to  $CO_2$  by  $O_2$ . Therefore, the following reactions



as well as the development of catalysts that favor  $CH_4$  oxidation in the presence of  $SO_2$  and  $O_2$  have been a major subject of research. In previous work, we studied the oxides of some transition metals ( $Co$ ,  $Ni$ ,  $Fe$ ,  $V$ ,  $Mn$ ,  $Cr$ , and  $Mo$ ) supported on alumina [1] in order to determine the best surface for capturing  $SO_2$ . We found that the best adsorbent is  $Cr_2O_3/Al_2O_3$  [2, 3], which also catalyzes  $CH_4$  oxidation to obtain  $CO_2$ . It was selected due to its thermal and mechanical resistance and its possibility to be regenerated. We also experimentally determined the activation energies of the aforementioned reactions on  $Cr_2O_3/Al_2O_3$  under stoichiometric conditions [4]. We concluded that the presence of  $SO_2$  favors  $CH_4$  oxidation, decreasing the activation energy. In this paper, we present theoretical results based on the density functional theory on the adsorption and dissociation of diverse species involved in reactions (1)–(3) on  $Cr_2O_3/Al_2O_3$ . We aim to provide additional theoretical information to understand the mechanism of the oxidation reaction of  $CH_4$  on  $Cr_2O_3/Al_2O_3$  in the presence of  $SO_2$  and  $O_2$ .

## 2 Theoretical

First-principles total energy calculations were performed using DFT+U to investigate individual and simultaneous adsorption of  $SO_2$ ,  $CH_4$  and  $O_2$  molecules on the  $\alpha - Cr_2O_3(0001)$  surface as implemented in the Vienna Ab initio Simulation Package (VASP) code.

The  $\alpha - Cr_2O_3(0001)$  surface has been studied using different theoretical approaches [6, 7, 8, 9, 10, 11]. There is general agreement among the different methods that the surface undergoes strong vertical relaxations. In this paper, we take into account the strong correlation effects described by a Hubbard-type on-site Coulomb repulsion, not included in a density functional description [10]. The (0001) face was selected because in its natural state,  $Cr_2O_3$  has this type of structure in 97.20% of its volume, which is maintained up to temperatures of about 973K.

The Kohn-Sham equations were solved using projector augmented wave (PAW) method and a plane-wave basis set including plane waves up to 400 eV. Electron exchange and correlation energies were calculated within the local spin density approximation (LSDA) in the Perdew-Zunger form. The DFT+U method was used with values  $J=1$  and  $U=5$  [10]. Convergence is considered achieved when the forces on the ions are less than 0.03 eV/Å. Periodic boundary conditions are applied in the three perpendicular directions. The Hessian matrix of second derivatives was determined for ground structures within the harmonic approximation by two-sided finite differences, using a displacement step of 0.01 Å. Adsorbed atoms were displaced in the calculations, and diagonalization of the dynamic matrix yields the harmonic frequencies.

The surface is modelled as a rhomboid supercell with an edge size of 4.954 Å and 20 Å high. Each substrate layer is composed of one chromium atom, three oxygen atoms and one chromium atom, and is 2.263 Å thick. However, hereafter each layer composed of one type of atom only will be called a layer. The supercell used is shown in Fig. 1, while the geometric parameters obtained after surface optimization are listed in Table 1.

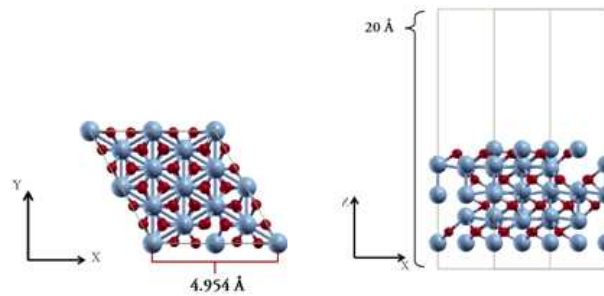


Figure 1:  $Cr_2O_3(0001)$  supercell.

The first Brillouin zone was sampled with a  $(3 \times 3 \times 1)$  gamma point centered mesh and only the gamma point was used for the cubic supercell used for the optimization of isolated molecules [3].

The adsorption energy of each adsorbate molecule is calculated as

Interlayer spacing	DFT+U LSD	GGA
$Cr_1 - O_2$	-61	-53
$O_2 - Cr_3$	+6	+14
$Cr_3 - Cr_4$	-44	+70
$Cr_4 - O_5$	+9	+12
$O_5 - Cr_6$	-2	+12
$Cr_6 - Cr_7$	+7	-56
$Cr_7 - O_8$	-2	+10
$O_8 - Cr_9$	-1	-5
$Cr_9 - Cr_{10}$	+3	-5

Table 1: Variation in atomic interlayer spacings of the  $\alpha - Cr_2O_3(0001)$  substrate after surface optimization. The initial spacings are:  $Cr - O = 0.94\text{\AA}$ ,  $Cr - Cr = 0.38\text{\AA}$ . Comparison of the results from DFT, LSDA and GGA methods.

$$E_a = E(Adsorbate/Cr_2O_3) - E(Adsorbate) - E(Cr_2O_3) \quad (4)$$

The first term is the energy of the optimized configuration for the relaxed adsorbate molecule bonded to the clean surface. The second term is the energy of the optimized gas-phase adsorbate molecule (isolated), and the third term is the energy of the optimized surface. Based on this definition, negative values of  $E_a$  correspond to stable configurations. The structures of each isolated molecule were optimized first; they are called “simple systems”:

- $SO_2$  on  $Cr_2O_3(0001)$
- $CH_4$  on  $Cr_2O_3(0001)$
- $O_2$  on  $Cr_2O_3(0001)$
- $S$  on  $Cr_2O_3(0001)$
- $CO$  on  $Cr_2O_3(0001)$
- $CO_2$  on  $Cr_2O_3(0001)$

Using the results from the most stable geometries of these systems, molecules of other chemical species were adsorbed; they are called “compound systems”:

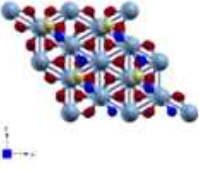
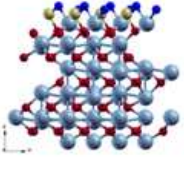
$E_a$ (eV)	X-Y Plane	X-Z Plane	$D[S - O_{ads}]$ (Å)	$D[S - Cr]$ (Å)
-3.09			1.51	1.77

Table 2: Most stable geometry of the  $SO_2$  system on  $Cr_2O_3$  optimized with the DFT+U formalism and its activation energy.

- $SO_2$  on  $O_2$  preadsorbed on  $Cr_2O_3(0001)$ .
- $CH_4$  on  $O_2$  preadsorbed on  $Cr_2O_3(0001)$ .
- $O_2$  on  $SO_2$ , preadsorbed on  $Cr_2O_3(0001)$ .

In a first stage, the calculations were performed using pseudopotentials based on the local density approximation (LDA) [5, 6]. Then, in order to achieve greater accuracy, pseudopotentials within the generalized gradient approximation (GGA) were used.

### 3 Results

#### 3.1 Simple systems: adsorbate on substrate

-  $SO_2$  on  $Cr_2O_3(0001)$ : after generating a clean surface and optimizing each isolated molecule, a  $SO_2$  molecule was adsorbed on the  $Cr_2O_3(0001)$  surface in different positions and geometries. The most stable configuration was found in previous studies [2] using the LDA pseudopotentials. The final results are listed in Table 2.

The adsorption of  $SO_2$  on the  $Cr_2O_3$  surface is a chemisorption process involving sulfite species formation and surface oxygen atoms: the sulfur atom binds to one surface oxygen atom, while sulfur dioxide oxygen atoms are bound to chromium atoms.

-  $CH_4$  on  $Cr_2O_3(0001)$ : one  $CH_4$  molecule was adsorbed on the  $Cr_2O_3(0001)$  surface in different positions and geometries. The most stable results, which are summarized in Table 3, indicate that no molecular adsorption occurred on the surface under study.

-  $O_2$  on  $Cr_2O_3(0001)$ : the most stable results for this system are shown in Table 4 and Fig. 2. The two atoms of the oxygen molecules are adsorbed on the same surface chromium atom.


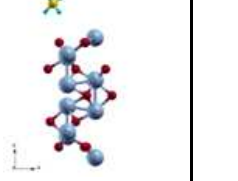
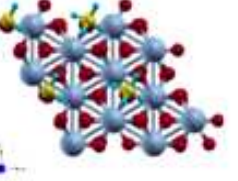
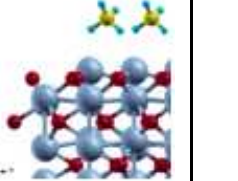

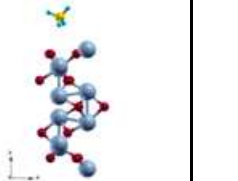
$E_a(\text{eV})$	X-Y Plane	X-Z Plane	$D[C - Cr_{sup}](\text{\AA})$	$D[H_1 - Cr_{sup}](\text{\AA})$	$D[H_2 - Cr_{sup}](\text{\AA})$
-0.0159			5.255	5.836	5.438
-0.0138			5.235	5.532	4.155
-0.014			3.783	4.752	4.124

Table 3: Most stable geometries of the  $CH_4$  system on  $Cr_2O_3$  optimized with the DFT+U formalism and their activation energies.

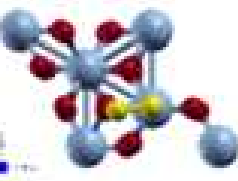
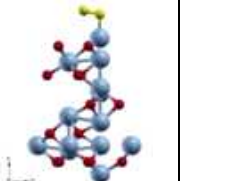
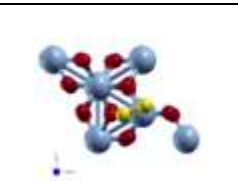
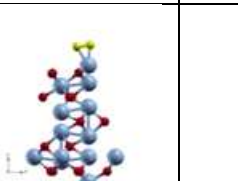
$E_a(\text{eV})$	X-Y Plane	X-Z Plane	$D[O_1 - O_2](\text{\AA})$	$D[O_1 - Cr_3](\text{\AA})$	$D[O_2 - Cr_2](\text{\AA})$
-0.478			1.214	3.054	2.136
-0.446			1.344	2.002	1.993

Table 4: Most stable geometries of the  $O_2$  molecularly adsorbed on  $Cr_2O_3$  optimized with the DFT+U formalism and their activation energies.

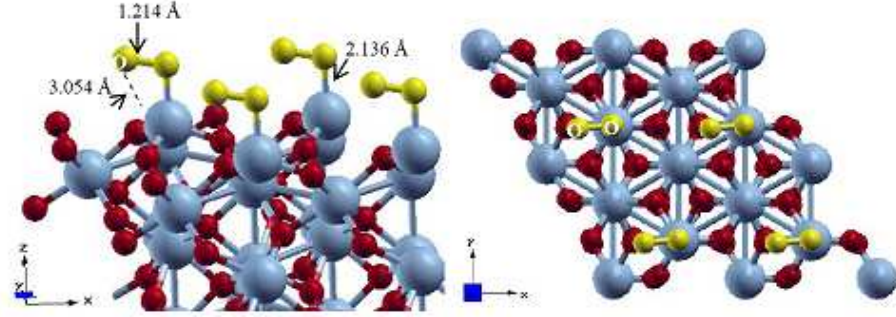


Figure 2: Geometric details of the first structure listed in Table 4.

$E_a$ (eV)	X-Y Plane	X-Z Plane	$D [O_1 - O_2] (\text{\AA})$	$D [O_1 - Cr_3] (\text{\AA})$	$D [O_2 - Cr_2] (\text{\AA})$
-0.474			2.466	1.585	3.85

Table 5: Most stable geometry of the dissociative oxygen adsorption on  $Cr_2O_3$  optimized with the DFT+U formalism and its activation energy.

- Dissociative  $O_2$  adsorption on  $Cr_2O_3(0001)$ : in this system, two  $O_2$  atoms were placed on the surface in order to study the stability of the adsorbate molecule and the possible availability of oxygen atoms to oxidize methane to  $CO_2$ . The most stable dissociative adsorption configuration shows both  $O_2$  atoms adsorbed on the same chromium atom in the first layer (see Table 5 and Fig. 3).

-  $S$  on  $Cr_2O_3(0001)$ : a sulfur atom was adsorbed on the  $Cr_2O_3(0001)$  surface at five sites: on one chromium atom of the first layer, obtaining the lowest adsorption energy of -0.594 eV; on a chromium atom of the third layer; and on an oxygen atom of the second, fourth and fifth layers [2, 5].

-  $CO$  on  $Cr_2O_3(0001)$ : one  $CO$  molecule was adsorbed on the  $Cr_2O_3(0001)$  surface, obtaining an adsorption energy of -2.33 eV in the most stable geometry [5].

-  $CO_2$  on  $Cr_2O_3(0001)$ : one  $CO_2$  molecule was adsorbed in different positions and geometries. The system obtained was more unstable than that of  $CO$  on the same surface, with an adsorption energy of -0.81 eV for the most stable geometry (see Fig. 5).

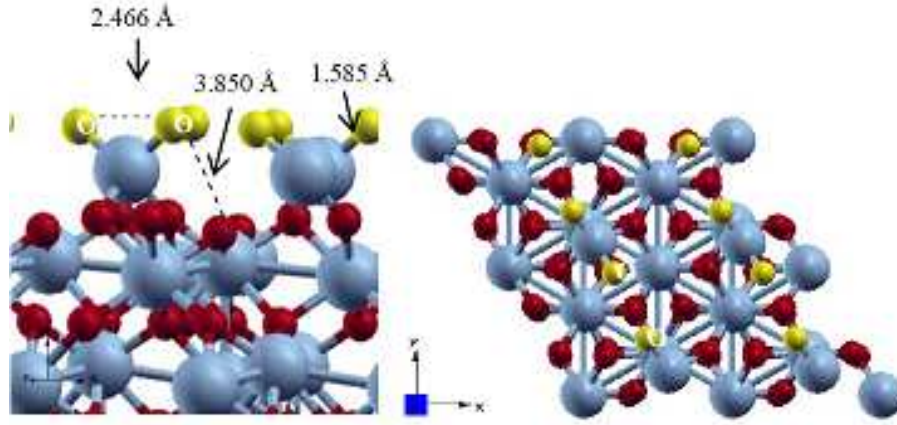


Figure 3: Geometric details of the first structure listed in Table 5.

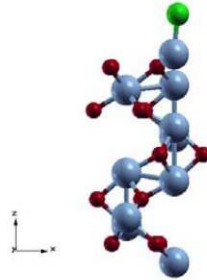


Figure 4: Most stable optimized structure of  $S$  adsorbed on the  $Cr_2O_3(0001)$  surface.

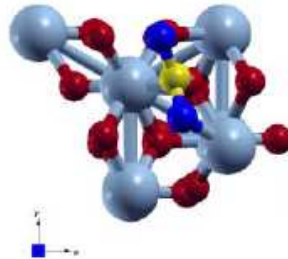


Figure 5: Most stable optimized geometry of  $CO_2$  adsorbed on the  $Cr_2O_3(0001)$  surface.



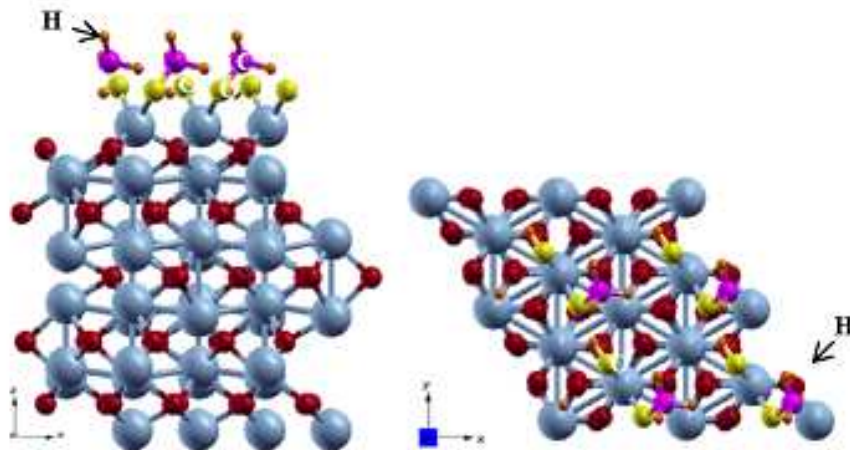


Figure 6: Most stable optimized geometry of  $CH_4$  on  $O_2$  dissociatively adsorbed on the  $Cr_2O_3(0001)$  surface.

### 3.2 Complex systems: adsorption of one species on another one preadsorbed on the substrate

After obtaining the most stable geometries for the adsorption of one molecule on the catalytic surface, we investigated the adsorption of one of the species under study on another one preadsorbed on  $Cr_2O_3(0001)$ . Thus, the interaction between gas species on the surface was examined, obtaining the adsorption energies of the most stable configuration, together with the bond lengths, the variations in the angles formed between the atoms of those species, and the new compounds formed once the interactions between them had ceased.

- $CH_4$  on an  $O_2$  molecule preadsorbed on  $Cr_2O_3(0001)$ : the adsorption of one methane molecule on the  $Cr_2O_3(0001)$  surface was studied using the most stable geometry for the adsorption of one  $O_2$  molecule. No stable geometry was found, indicating that methane does not adsorb on the  $O_2$  molecule adsorbed on  $Cr_2O_3(0001)$ .

- $CH_4$  on  $O_2$  dissociatively adsorbed on  $Cr_2O_3(0001)$ : a  $CH_4$  molecule was placed in different positions on an  $O_2$  molecule dissociatively adsorbed on the substrate. In this case, as in the above, the most stable geometry for the dissociative  $O_2$  adsorption on  $Cr_2O_3(0001)$  was used. The dissociation of the methane molecule was obtained, as well as the formation of  $OH$  species and methoxy groups ( $-O-CH_3$ ) as shown in Fig. 6.

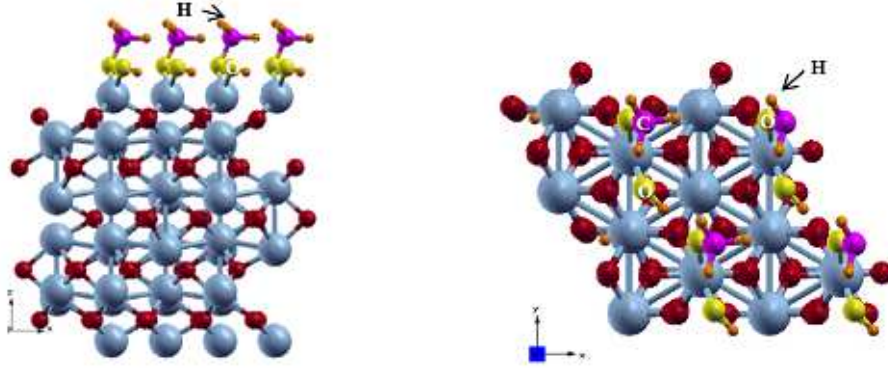


Figure 7: Adsorption geometry ( $E_a = -1.4982\text{eV}$ ) of  $\text{CH}_4$  on  $\text{O}_2$  dissociatively adsorbed on the  $\text{Cr}_2\text{O}_3(0001)$  surface.

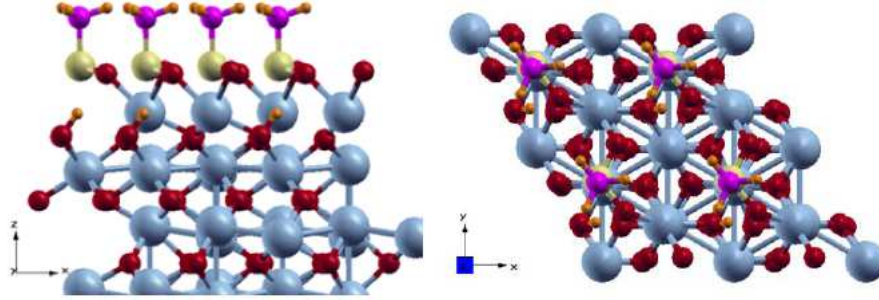


Figure 8: Most stable optimized geometry of  $\text{CH}_4$  on  $\text{SO}_2$  preadsorbed on the  $\text{Cr}_2\text{O}_3(0001)$  surface.

The most stable geometry has an energy of  $-1.7914\text{ eV}$ . The next energy found was  $-1.4982\text{ eV}$ , whose adsorption geometry is depicted in Fig 7.

-  $\text{CH}_4$  on  $\text{SO}_2$ , preadsorbed on  $\text{Cr}_2\text{O}_3(0001)$ : in the most stable geometry, with an energy of  $-0.2758\text{ eV}$ , a hydroxyl with an  $\text{O}$  atom of the third substrate layer is formed, while sulfur binds to the methyl group ( $\text{CH}_3$ ) and  $\text{SO}_2$  oxygen atoms to the surface  $\text{Cr}$  atoms, as shown in Fig. 8.

-  $\text{O}_2$  on  $\text{SO}_2$ , preadsorbed on  $\text{Cr}_2\text{O}_3(0001)$ : an adsorption energy of  $-1.00\text{ eV}$  was found for the most stable configuration; oxygen dissociation led to the formation of  $\text{SO}_3$  species on the surface.

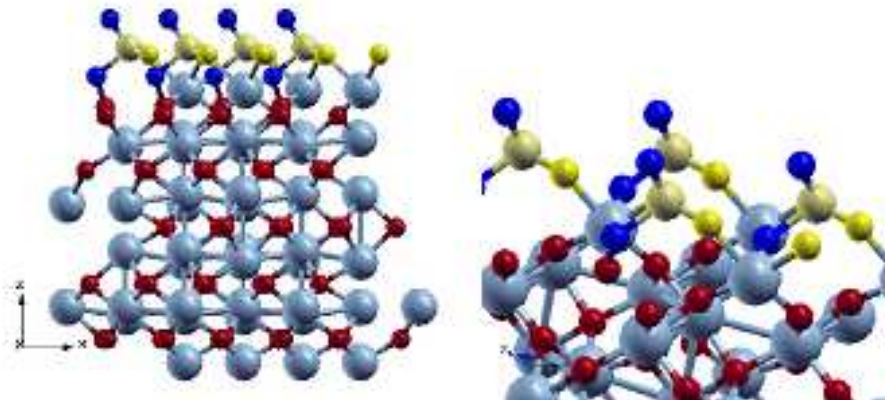


Figure 9: Most stable optimized geometry of  $O_2$  on  $SO_2$  preadsorbed on the  $Cr_2O_3(0001)$  surface.

## 4 Discussion and Conclusions

The adsorption of  $CH_4$  on  $Cr_2O_3(0001)$  is not stable; the presence of molecularly adsorbed oxygen does not favor adsorption. However, in the presence of sulfur dioxide or atomic oxygen,  $CH_4$  may decompose to form hydroxyl species, methyl groups adsorbed on sulfur and/or methoxy group ( $R-O-CH_3$ ) atoms.  $SO_2$  adsorption leads to the formation of sulfite species involving surface or preadsorbed oxygen atoms. No sulfate species formation was observed.  $O_2$  adsorption in the presence of  $SO_2$  favors oxygen dissociation to form sulfite species. Molecular and dissociative  $O_2$  adsorption occurs on this substrate with almost the same energy. The most stable configuration is obtained with the two atoms on the same  $Cr$  atom. The presence of  $SO_2$  favors the dissociative adsorption of oxygen to form sulfite species. In previous work [4] we experimentally showed that the activation energy of reaction (3) is lower than that of reaction (2) under stoichiometric conditions. The presence of  $SO_2$  would activate the catalyst surface favoring oxygen dissociation and methane decomposition. FTIR spectroscopy studies on samples of the catalysts used in reactions (2) and (3) allowed us to identify hydroxyl and methyl species as the ones found in this work, as well as additional products of methane dehydrogenations [5]. These results will be presented in a future paper together with further DFT calculations. The stability of the oxygen molecule adsorbed on the  $Cr_2O_3$  surface may affect the interaction of gas-phase  $SO_2$  with adsorbed oxygen and deserves a more detailed study to be included in a future publication. The size of the cell used in the calculations as well as periodic boundary conditions simulate experimental conditions with high adsorbate coverage. The experiments were also performed in a continuous-flow fixed-bed reactor under conditions that are not directly comparable to

theoretical conditions. Nevertheless, from previous comparisons with  $SO_2$  desorption, reliable conclusions from calculations based on DFT+U can be drawn [3]. Then, we conclude that these calculations may provide useful information on the elementary stages of reactions (1)–(3) in order to establish the reaction mechanism.

## 5 Acknowledgments

This work was supported by Consejo de Investigaciones Científicas y Técnicas (CONICET), Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), Universidad Nacional de La Plata and the Faculty of Chemistry and Engineering Fray Roger Bacon

## References

- [1] 1- I. Coria, S. Medina, I.R. Ramos, A.G. Ruiz, *Energieia* 1, 49-65 (2003).
- [2] I. D. Coria, O. Carattoli, S. Hernandez Guiance, Y. Malik, *Energieia* 5, 30-39 (2007).
- [3] 3- V.A. Ranea, S.N. Hernandez, S. Medina, I.M. Irurzun, I.D. Coria, E.E. Mola, *Surface Science* 605 489–493 (2011).
- [4] S. N. Hernandez Guiance, I. D. Coria, I. M. Irurzun, E. E. Mola, *Chemical Physics Letters* 660123-126 (2016).
- [5] S. N. Hernández Guiance. Estudio Teórico-Experimental de la Adsorción y Reducción Catalítica de  $SO_2$  sobre  $Cr_2O_3/Al_2O_3$  en Presencia de  $CH_4$  y  $O_2$  a Altas Temperaturas. Tesis Doctoral, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, (2016).
- [6] M. Catti, G. Sandrone, G. Valerio, R. Dovesi, *J. Phys. Chem. Solids* 571735-1741(1996).
- [7] M.S.M. Barrera, J.F. Sanz, L. Alvarez, J. Odriozola, *Phys. Rev. B* 58 6057-6062 (1998).
- [8] J. Cline, A. Rigos, T. Arias, *J. Phys. Chem. B* 104 6195-6201 (2000).
- [9] X. Wang, J. Smith, *Phys. Rev. B* 68 201402 (2003).
- [10] A. Rohrbach, J. Hafner, G. Kresse, *Phys. Rev. B* 70125426 (2004).
- [11] S. N. Hernández Guiance. PhD Thesis. University of La Plata, Buenos Aires, Argentina, 2016.